3D printing of solid-state Li batteries

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Overview

Timeline

- Start date: Nov. 2018
- End date: Feb. 2022
- Percent complete: 50%

Barriers

- **Performance**: The integration of ceramic solid state electrolyte into solid state batteries is challenging due to the brittleness, air-sensitivity, and poor solid-solid contact issues.

Budget

- Total project funding:
    - DOE share: $1.125 M
- FY20 Funding: $360K

Partner

- Simulation group:
    - Brandon C. Wood (PI)
    - “Integrated multiscale model for design of robust 3D solid-state lithium batteries”

Relevance

- **Impact**
  - Unlike the well-established roll-to-roll fabrication of conventional Li-ion batteries, the processing of SSBs is unique due to the brittleness of solid-state electrolytes (SSEs).
    - Commercial SSE separators are ultrathick, which limits power and energy densities.
    - Free-standing ultrathin ceramic separators are mechanically fragile.

- **Strategies:** 3D printing enables
  - Multi-component integration
  - Interfacial engineering: morphological, chemical and mechanical control

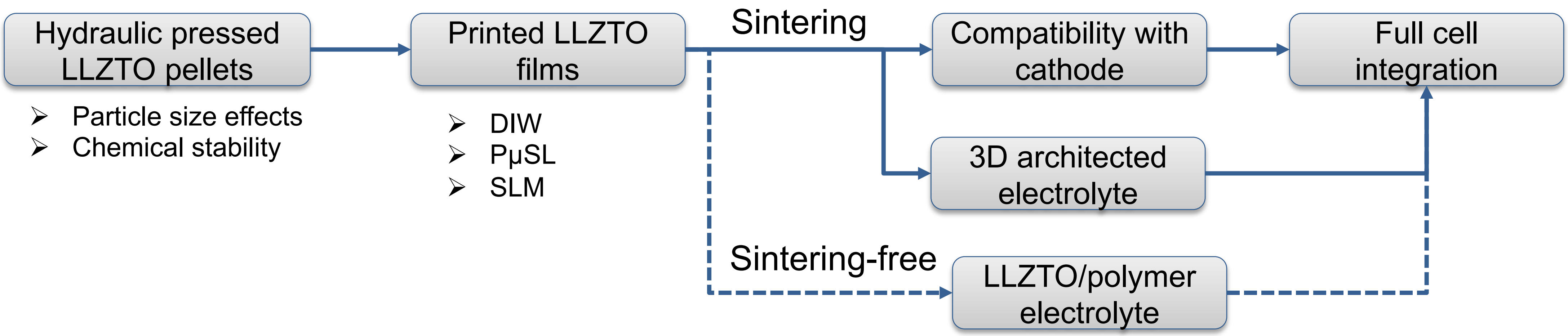
- **Objectives**
  - Tuning microstructures of 3D printed SSE separators
    - Printability & conductivity, grain structure & porosity
  - Process compatibility with cathode printing
    - Sintering conditions and materials selection
  - 3D printing of sintering-free SSE separators
    - SSE/polymer composite

Milestones

- FY20
  - Q1: ALD on ball milled electrolyte/electrode powders (completed)
  - Q2: Measure thermochemical stabilities of electrolyte-electrode-conductive additive mixtures (in progress)
  - Q3: Measure the impedance of the sintered mixtures
  - Q4: Evaluate cell stability and failure mechanisms
- FY21 (planned)
  - Q1: 3D printed architected LLZTO electrolyte
  - Q2: Enhancement of cell performance from co-sintering approach
  - Q3: 3D printed LLZTO/polymer composite electrolyte
  - Q4: Evaluation of LLZTO/polymer composite electrolyte

Approach

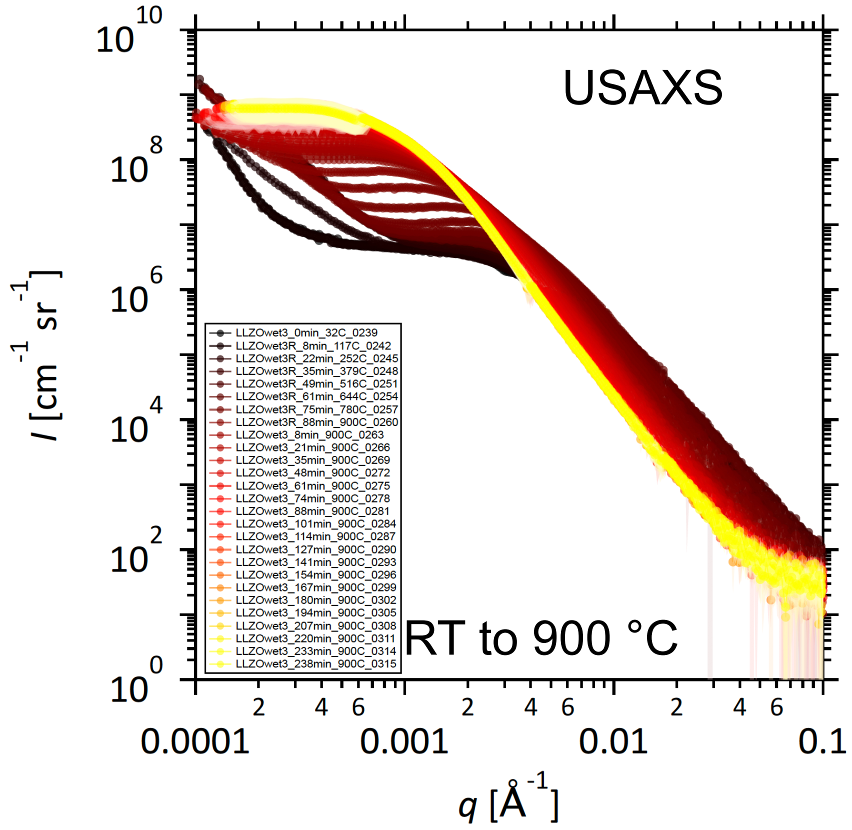
- Starting from easily prepared hydraulic pressed pellets, identify particle size effects and chemical stability, which serve as guidelines for ink preparation.
- Explore a few 3D printing techniques including direct ink writing (DIW), projection microstereolithography (PμSL), and selective laser melting (SLM) are explored to prepare thin dense cubic LLZTO films with high ionic conductivity and low charge transfer resistance.
- Investigate co-sintering compatibility with cathodes in order to integrate separator and cathode together in the 3D printing step.
- As a backup plan, integrate cathodes after the preparation of freestanding 2D/3D architected LLZTO separators. Develop proper inks to directly print ionically conducting LLZTO/polymer composite electrolytes.

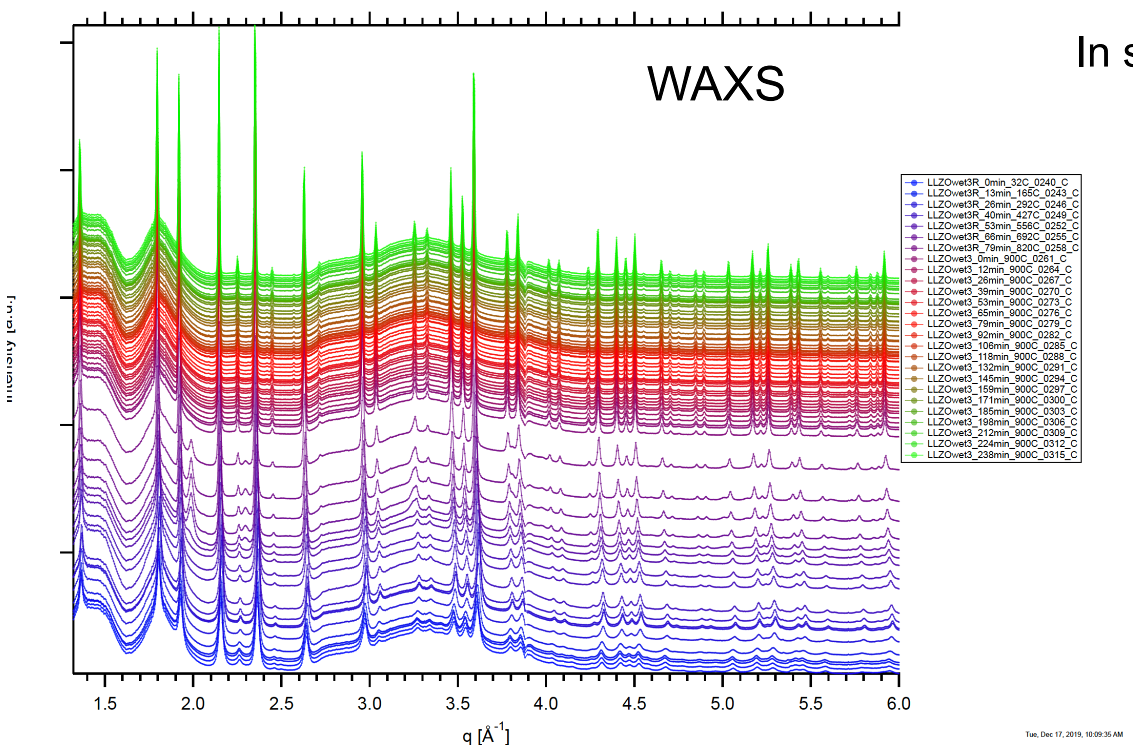


Accomplishments to date – FY20

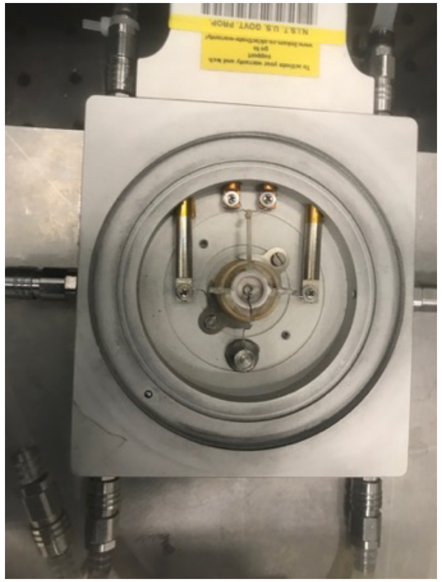
- Thermal stability of LLZTO
  - In situ USAXS/WAXS studies
  - Ex situ XRD analysis of printed films vs pressed pellets
- Thermal stability of LLZTO with additives
  - Lower charge transfer resistance was achieved using Al_2O_3 coated LLZTO powders
  - Lower sintering temperature for printed films was achieved via the addition of Li_3BO_3 sintering agent.
- Co-sintering with cathode materials
  - This effort is still under development

In Situ USAXS/WAXS studies on sintering of LLZTO





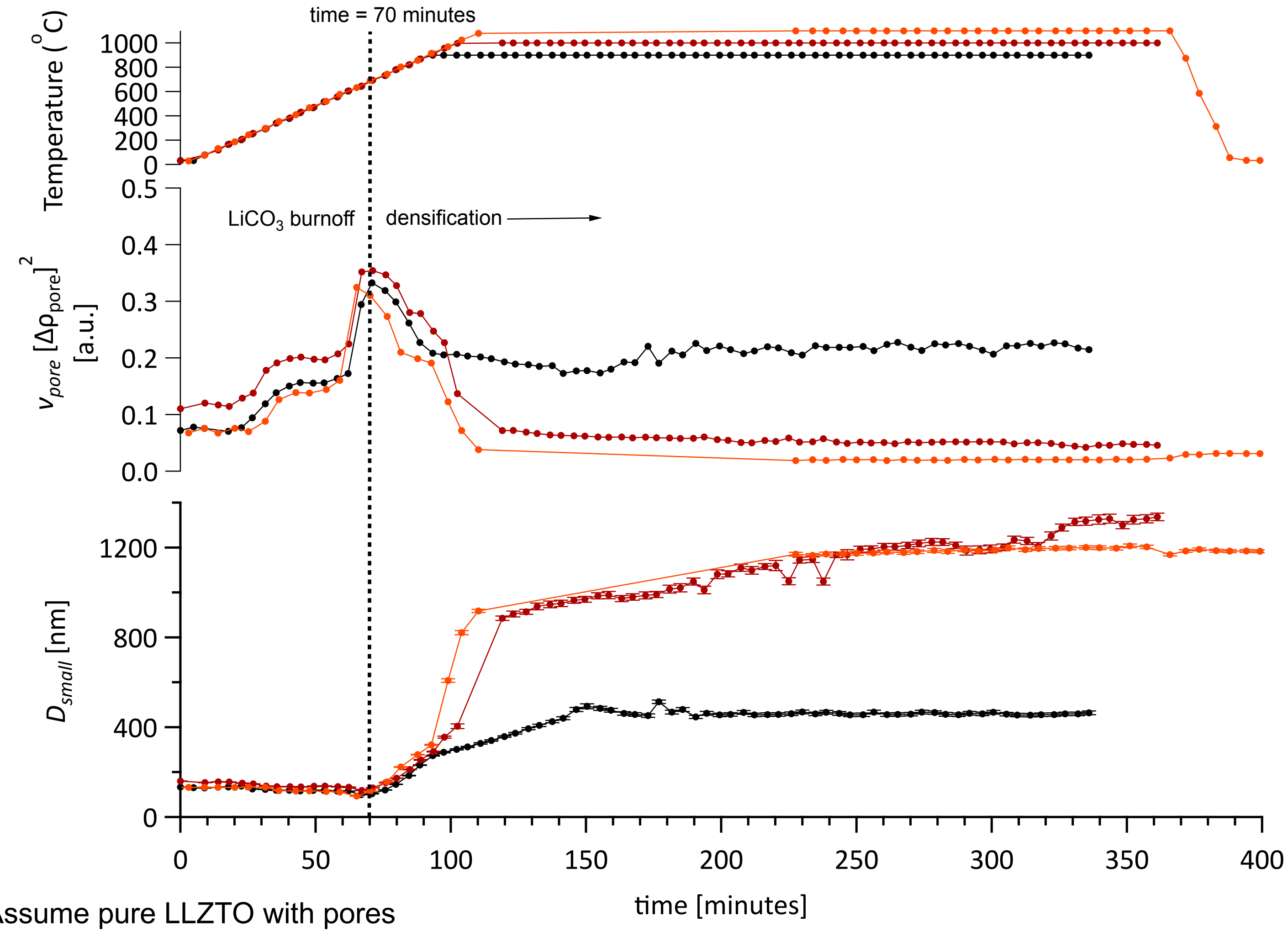
In situ Linkam heating stage



Espitia, Hammons, etc. In preparation

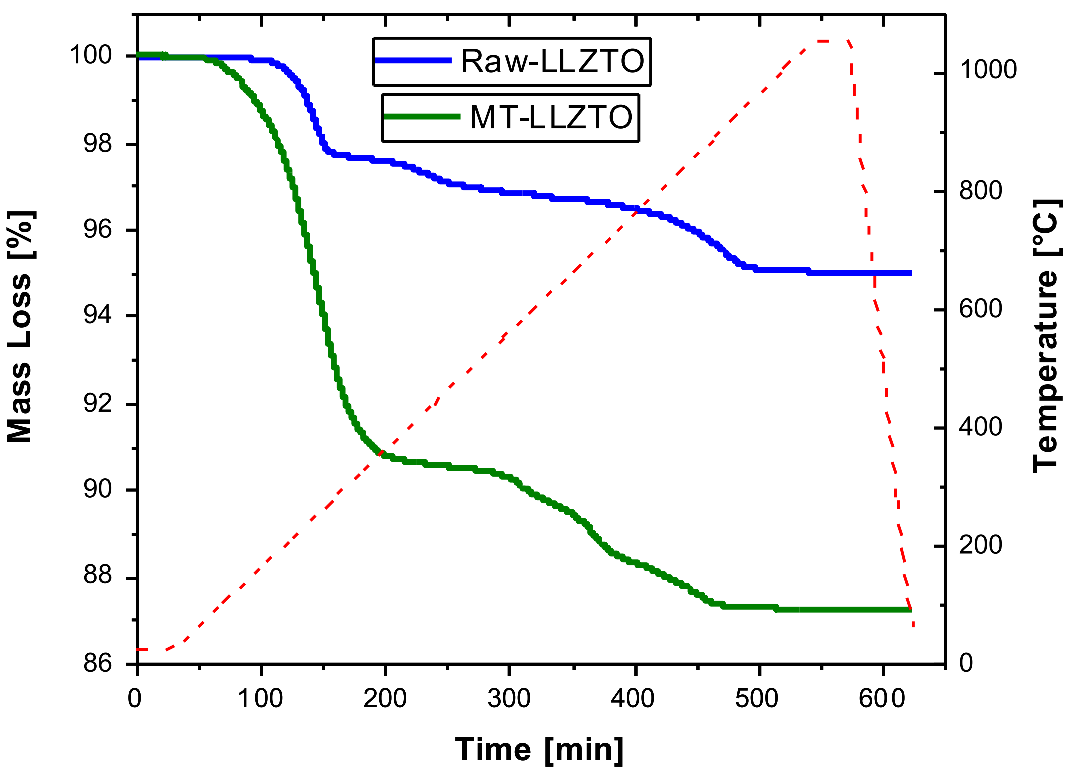
- Pore and phase changes as a function of temperature and time were captured in situ at APS synchrotron beamline, which is the first step to understand co-sintering behavior.

In situ USAXS reveals porous nature as a function of temperature and time

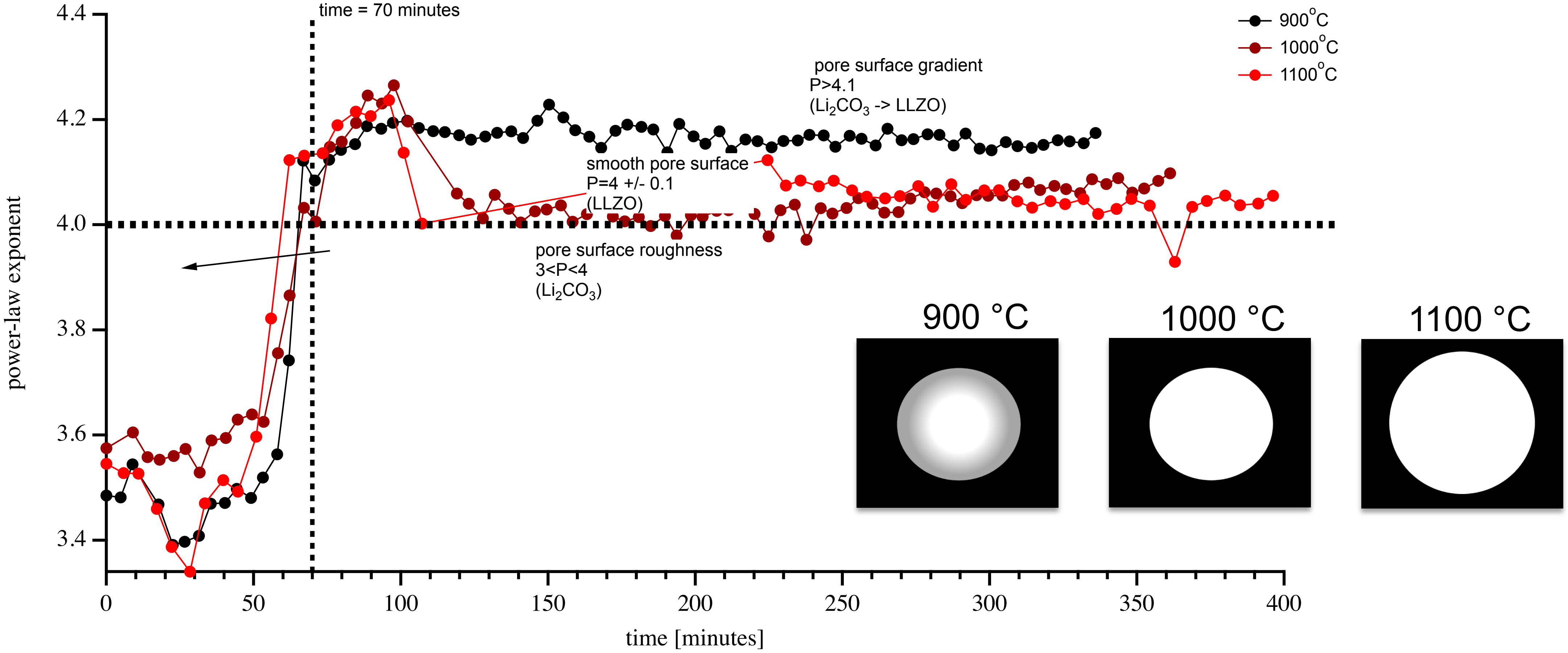


* Assume pure LLZTO with pores

- TGA reveals the mass loss due to proton/H_2O and CO_2 removal.

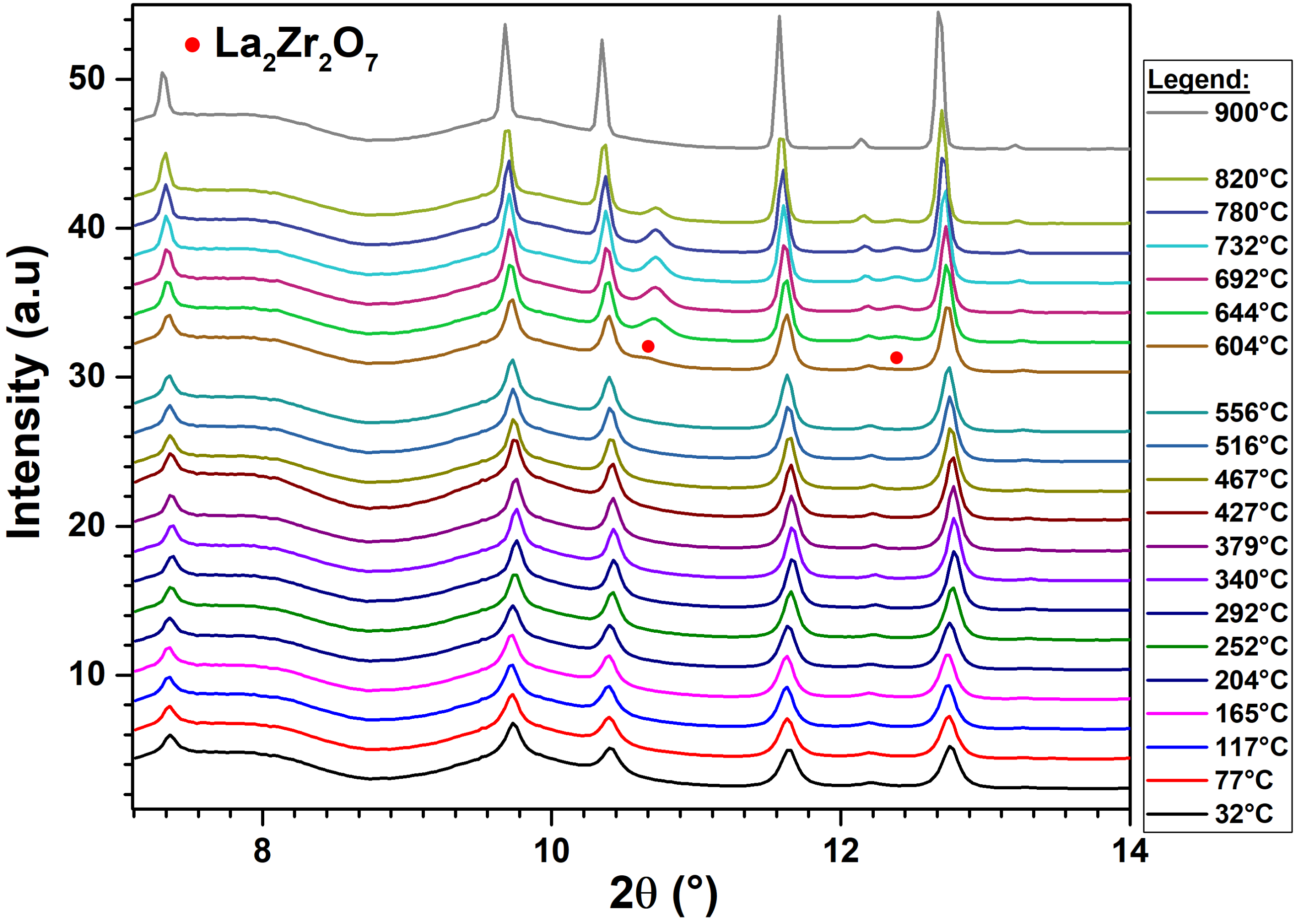


Change of shape and gradient structure of the pores



- Smoothening of roughed surface is observed from 50-70 min (500 °C to 700 °C).
- Overshooting to 4.2 indicates surface chemical gradient, which vanishes above sintering temperature of 1000 °C.

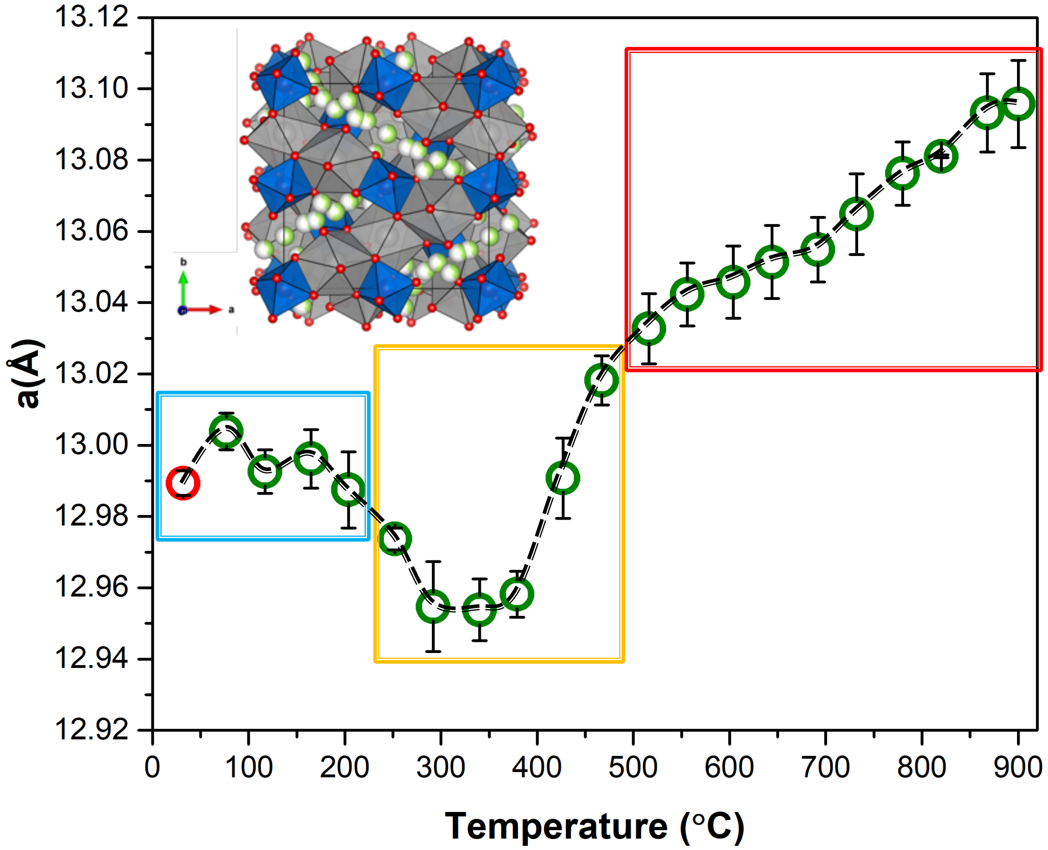
WAXS diffraction patterns of *in situ* LLZTO from 32°C to 900°C

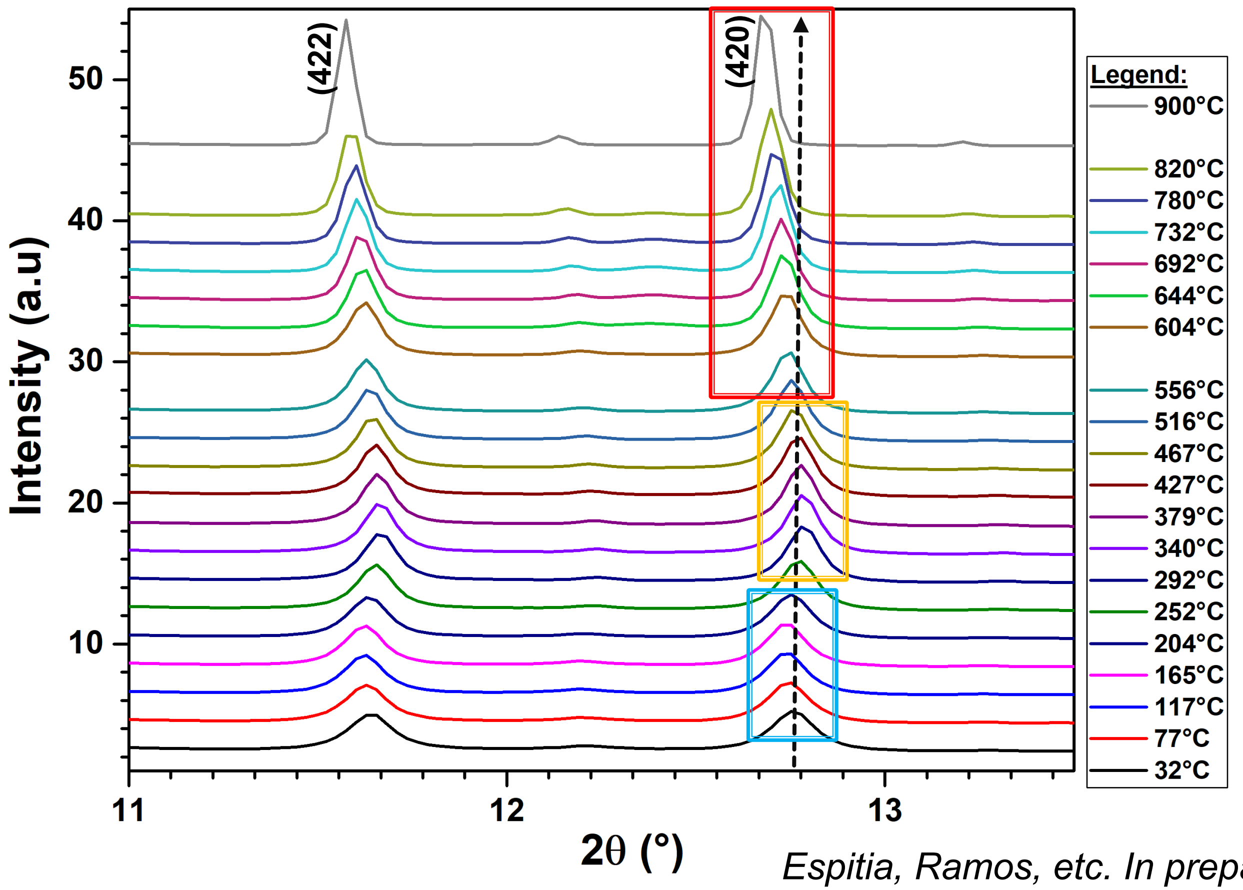


Espitia, Ramos, etc. In preparation

- $La_2Zr_2O_7$ phase forms at ~ 600 °C and disappears at ~ 870 °C.

Evolution of lattice constant and *in situ* WAXS diffraction patterns of LLZTO from 32°C to 900°C



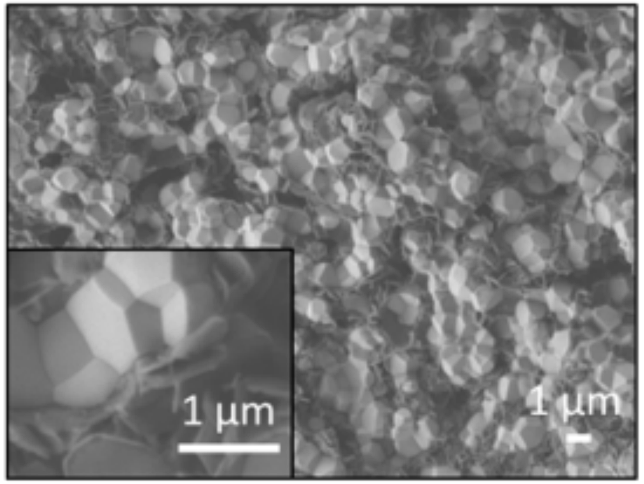


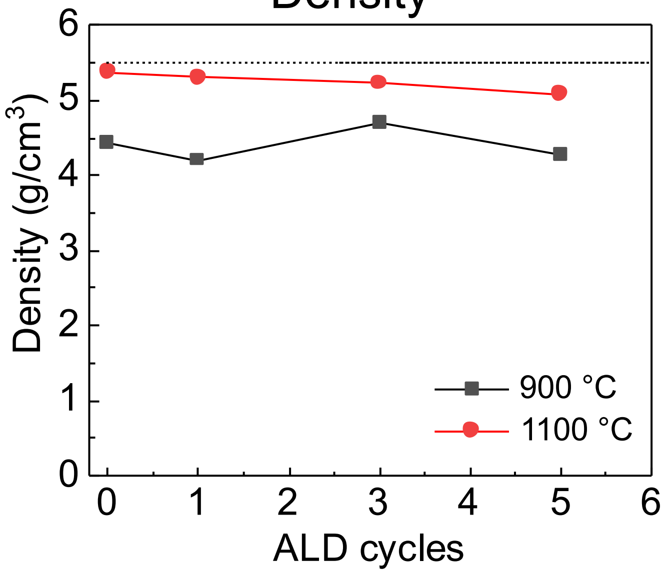
Espitia, Ramos, etc. In preparation

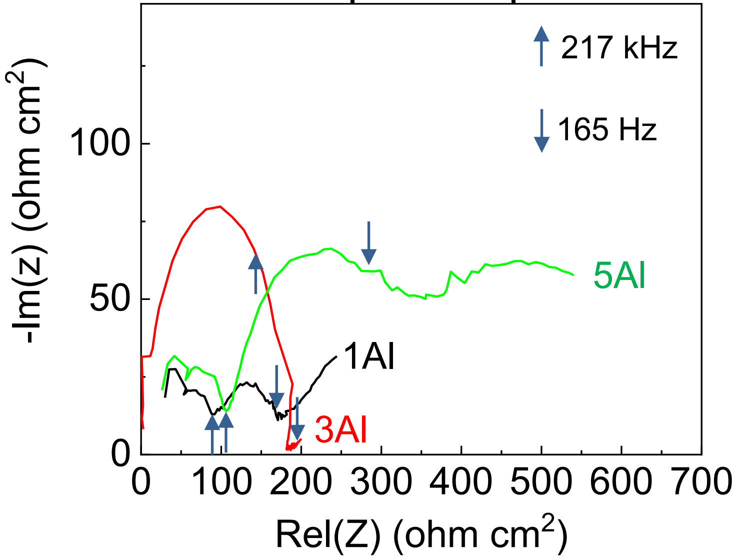
- Due to air exposure of the ball milled powders prior to sintering, proton/Li^+ exchange leads to lattice expansion at room temperature.
- From ~ 100 °C up to 350 °C, protons are removed, leading to lattice shrinkage.
- Above 500 °C, thermal induced expansion slows down, which may be related to the decomposition of LLZTO into $La_2Zr_2O_7$ and other related phases.

Powder ALD: one cycle of Al_2O_3 modification of ball-milled LLZTO powders results in dramatically improved surface charge transfer properties

SEM: 1 cycle Al_2O_3_900 °C



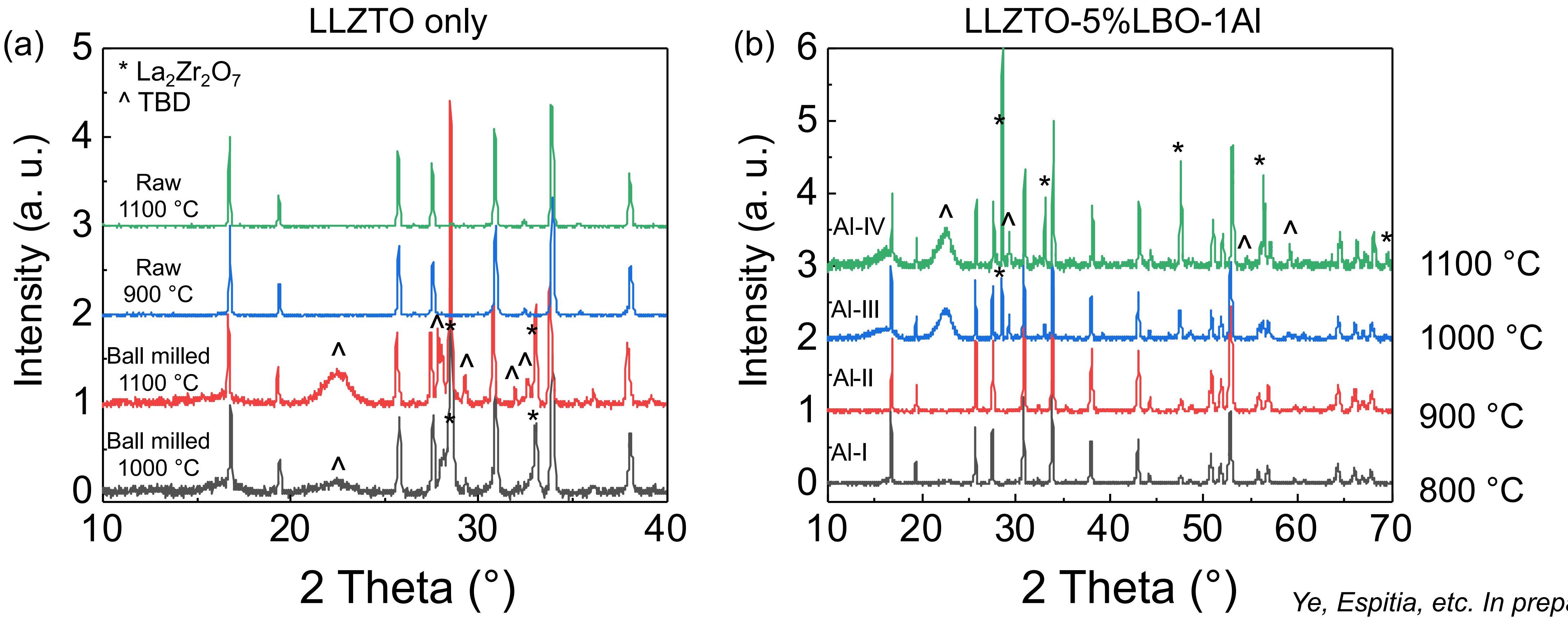




Espitia, Ye, etc. In preparation

- Al_2O_3 coating may have slightly hindered densification as indicated from density measurement.
- However, contact with Li is dramatically improved and charge transfer resistance < 100 ohm cm^2 is achieved for pellets sintered at 900 °C.

PµSL printed film: ALD Al_2O_3 modification on LLZTO-5%LBO milled powders

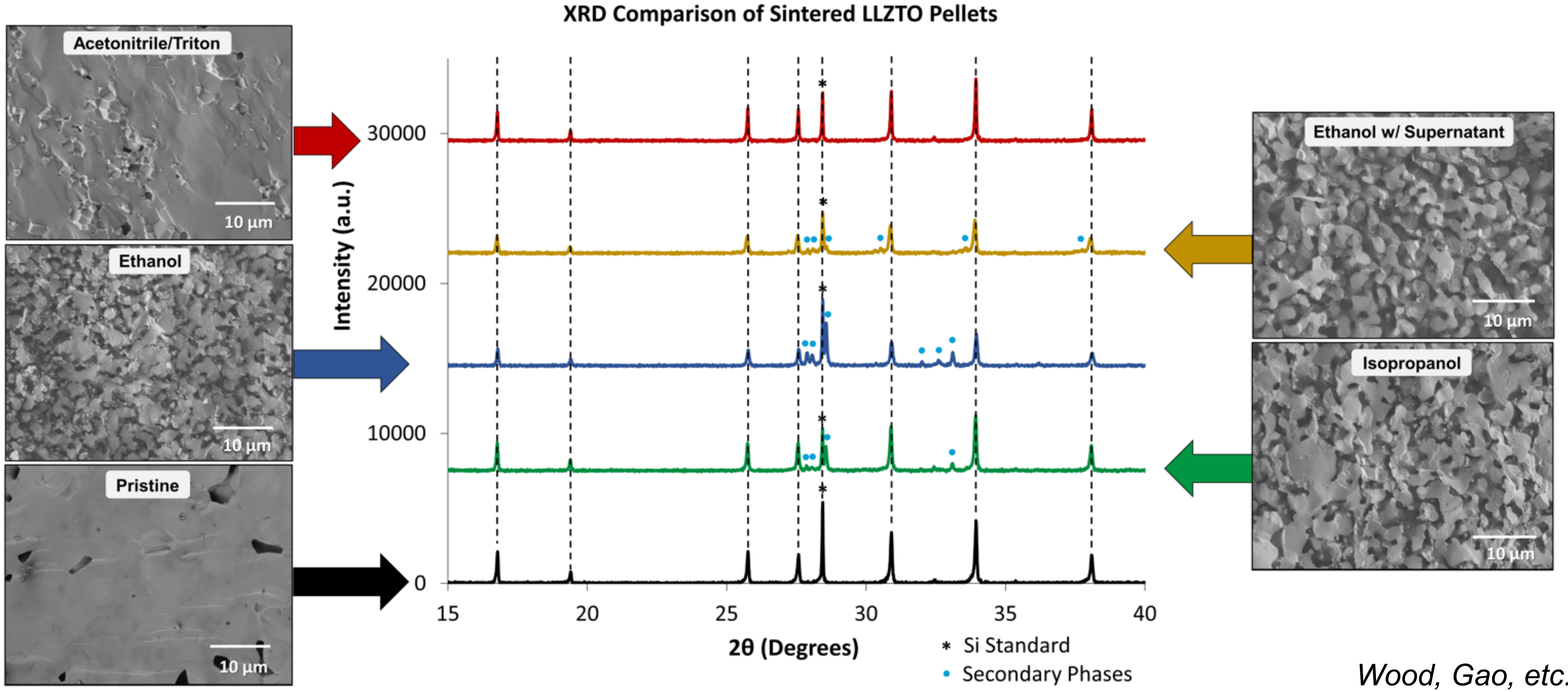


Ye, Espitia, etc. In preparation

- Smaller particle size is less stable above 1000 °C, probably due to low packing density that facilitates Li loss.

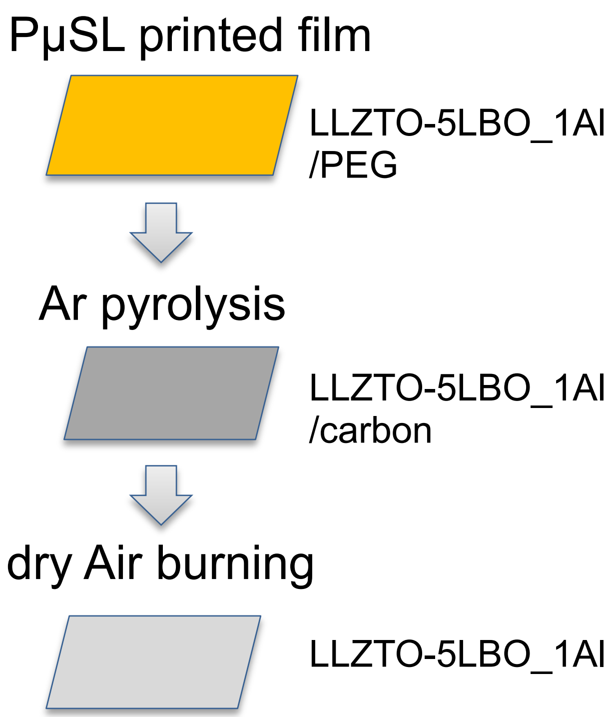
Hydraulic pressed pellets show different sintering stability

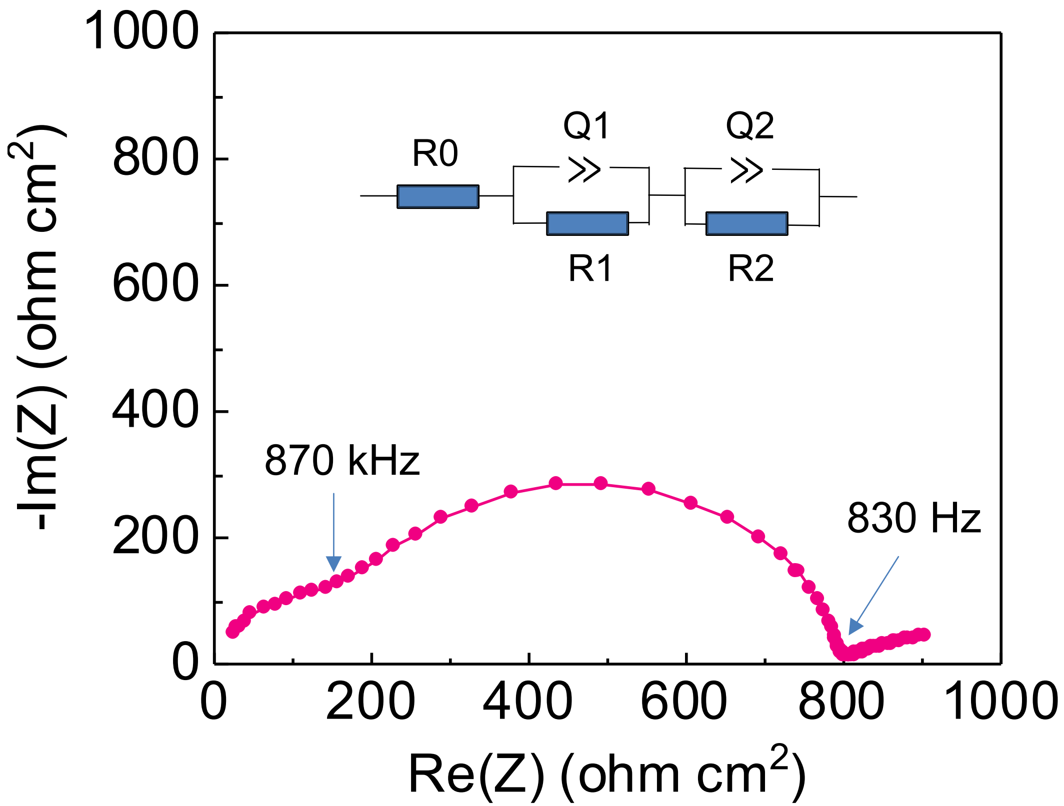
- Powder preparation: pristine *vs* powders high-energy ball milled in different liquids.
- Sintering condition: 1100 °C 6h in Ar



Wood, Gao, etc. In preparation

EIS of PμSL printed film after post processing





- Flat, dense, thin film with ionic conductivity of 7.6×10^{-5} S/cm and charge transfer resistance of 314 ohm cm^2 obtained at 900 °C sintering temperature.

On-going efforts: Co-sintering of cathode/LLZTO

Cathodes/LLZTO pellets

Thermal stability

- Narrow down the chemistry and particle size

→

Cathodes/LLZTO films

Thermal stability

- Find optimal sintering condition

→

Bilayer printing and post processing

- Improve interfacial stability

→

Full cell assembly and testing

- Evaluate cycling performance

Responses to Previous Year Reviewer's Comments

- The project was not reviewed last year.

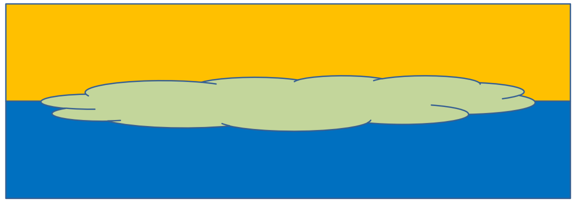
Partners/Collaborators

- Collaborating with LLNL simulation group via projects BAT426 and BAT403 led by **Dr. Brandon Wood** for multiscale validation and interpretation.
  - <u>First-principles simulation</u>
    - Doping effects on sintering temperature (**Dr. ShinYoung Kang**)
    - LLZO/LCO co-sintering stability (**Dr. Sabrina Wan**)
  - <u>Phase field modeling</u>
    - Sintering kinetics (**Dr. Rongpei Shi**)
    - Microstructure effects on ionic conductivity (**Dr. Tae Wook Heo**)
  - <u>Cell-level electrochemical modeling</u>
    - Predicting electrochemical impedance spectroscopy (**Dr. Aniruddha Jana**)

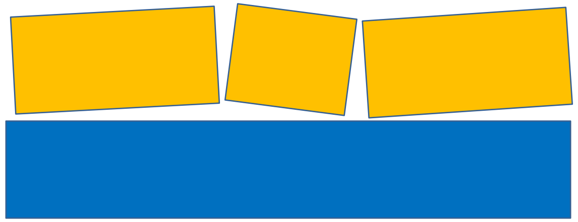
Remaining Challenges and Barriers

- Intimate incorporation of cathode electrodes with LLZTO electrolyte will be developed to avoid undesired side reactions and large strain mismatch that could impede ionic transport and mechanical integrity.

Bad reactions



Delamination, cracking



Ideal interface

- Strategies:
  - Tune particle size of different components
  - Add sintering agents to reduce sintering temperature
  - Add artificial interface to enhance contact
  - Use multiple step vs single step processing

Proposed Future Research

- **FY20**
  - Narrow down the choice of electrolyte-electrode-conductive mixtures via investigation of thermochemical/thermomechanical stability. Use morphology (SEM), phase (XRD) and conductivities (EIS) as benchmarks.
  - Evaluate cycling stability and identify failure mechanisms.

- **FY21**
  - Improve cycling stability by adjusting chemistry, interfacial architecture, and processing conditions.
  - Develop alternative pathways, including selective laser melting/sintering, and 3D Printing of LLZTO/polymer composite electrolyte.

Any proposed future work is subject to change based on funding levels.

Summary

- **Accomplishments**
  - Thermal stability of LLZTO pellets upon sintering was investigated using in situ USAXS/WAXS techniques.
  - Thermal stability of printed LLZTO films upon sintering was analyzed by XRD.
  - Thin, dense, and flat LLZTO films with good ionic conductivity and low charge transfer resistance towards Li were developed via PµSL printing and relatively low-temperature post processing.

- **Highlights**
  - In situ USAXS/WAXS provides unique capabilities to reveal sintering mechanisms.
  - 1 cycle of Al_2O_3 ALD coating on milled LLZTO powders can dramatically improve charge transfer properties.
  - Printed films and hydraulic pressed pellets may have very different sintering stabilities, especially for small particles.